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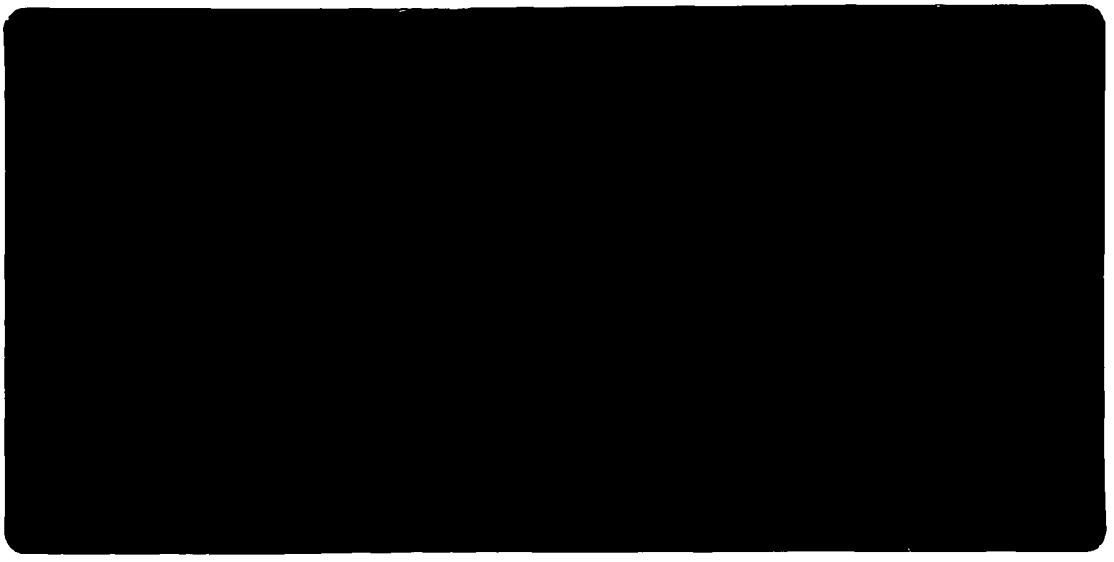

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KINETICS OF NO DEPLETION BY REACTION WITH MOLTEN SODIUM SPECIES

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Abstract

Thermodynamic calculations have shown that nitric oxide (NO) can potentially react with many sodium species that are present in kraft recovery furnaces. This study presents results of an investigation of the kinetics of NO depletion by reaction with molten sodium species. Experiments have been conducted in which NO in helium is bubbled through molten sodium carbonate. Preliminary results show a 10-70% reduction of NO over the temperature range of 860-970 °C. The depletion of NO appears to behave according to first-order reaction kinetics.

Introduction

In order to predict NO_x emissions from a kraft recovery furnace, one must understand both the rate of formation and the rate of depletion of the NO_x species. In a previous paper, it has been suggested that the reaction of NO with different sodium species could provide a depletion mechanism which is unique to kraft recovery furnaces.[1]

Many reactive sodium species are present in a kraft recovery furnace. These species exist in different phases depending on location (as temperature varies with location in the furnace). In the lower furnace, molten smelt is a source for volatilization of sodium species which form fume.[2] At this point, the potential for reactions between NO_x species and the molten smelt exists. Above the smelt bed, and traveling up the furnace, vapor phase alkali species (e.g., Na and Na_2O) could potentially react with NO_x before precipitating as fume. In the upper furnace, it is understood that solid fume particles react with SO_2.[3] These fume particles could also react with NO_x.

Nitrogen analysis of industrial smelt samples are shown below in Table 1.

Table 1: Nitrogen Analysis of Industrial Smelt Samples

Smelt Sample	Nitrogen Content (% by wt.)
Mill A	0.003
Mill B	0.015
Mill C[4]	0.02
Mill C with biosludge[4]	0.24

The addition of the biosludge to the black liquor at Mill C resulted in slightly higher NO_x emissions and a significant increase in the nitrogen content of the smelt.[4] No data were available for NO_x emissions from mills A and B. The presence of nitrogen in smelt could feasibly be a reaction product, such as $NaNO_3$, or could simply be residual nitrogen compounds originating from the black liquor.

While thermodynamic calculations have shown that NO can react with Na_2CO_3, it is not known how fast or to what extent this reaction can occur in a recovery furnace. For this reason, experimental work has been initiated to determine the rate of reaction of NO with molten Na_2CO_3.

Experimental Apparatus

Experiments have been conducted in which NO is bubbled through molten sodium carbonate. The experimental apparatus is depicted below in Figure 1.

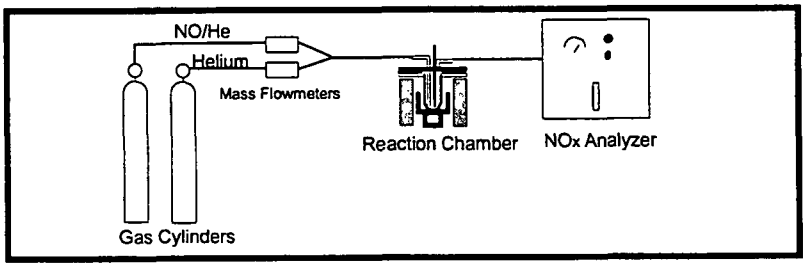

Figure 1: Experimental Apparatus

Helium and a mixed gas of nitric oxide in helium (1850 ppm NO) are fed from pressurized gas cylinders. Flow is measured by Hastings-Teledyne™ digital mass flowmeters and is controlled manually by needle valves. The gas is fed to the reaction chamber which is described in more detail below. Exit gas from the system is analyzed by a chemiluminescent NO_x analyzer.

Molten salts are contained in a 5-inch alumina crucible which is cemented to a stainless steel flange. A graphite gasket is placed between the flange and the lid which is held in place by eight bolts to form a gas-tight seal. The reaction vessel is heated by a tube furnace. Gases are bubbled through the salt using a 0.25-inch OD alumina tube. A type-K thermocouple, protected by an alumina well, is used to measure the temperature of the molten salt. The mass flowmeters, thermocouple, and NO_x analyzer are connected to a personal computer for data acquisition.

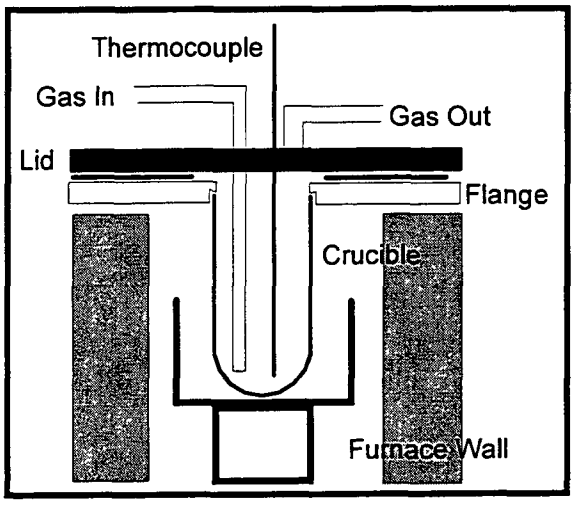

Figure 2: Reaction Chamber

Experimental Conditions

Gas flow rate, initial NO concentration, temperature, and the mass of salt in the system have been selected as independent variables in this study. Conditions for the set of six experiments are listed below in Table 2.

Table 2: Independent Variables for Experiments 1-6

Variable	Range
Mass of Na_2CO_3	17.5 and 30.0 g
Flow Rate	.75 and 1.0 L/min
Temperature	850-1000 °C

Each experimental condition is run for 6-9 minutes. Data for the flow rate, temperature and NO exit concentration are averaged over the last 2 minutes of this time interval. This allows the system to reach a steady state before averaging data.

Results

Raw data from the first set of experiments are plotted below in Figure 3. These data show the exit concentration decreasing as temperature increases. While the data are somewhat spread out, the overall trend is the same for each experiment.

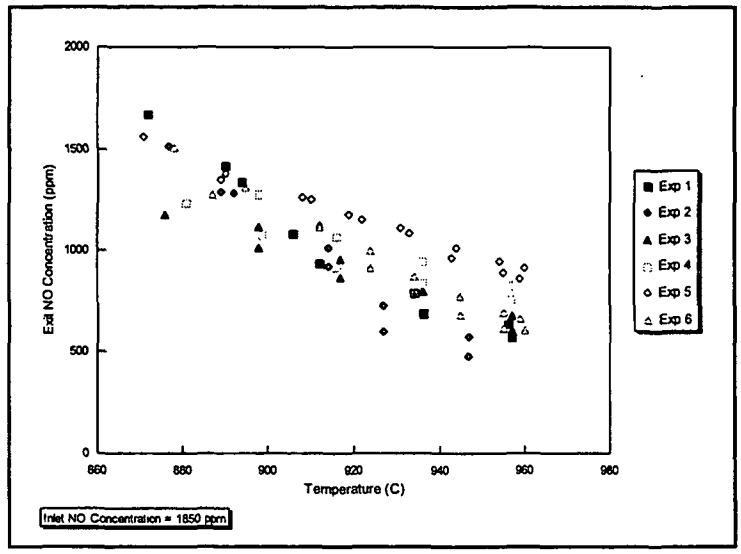

Figure 3: Exit Concentration as a Function of Temperature
Experiments 1, 2, and 6 use 35.0 g of Na_2CO_3;
Experiments 3, 4, and 5 use 17.5 g of Na_2CO_3.

Figure 4 shows a plot of the fractional conversion as a function of temperature. The conversion is calculated as:

$$X = 1 - \{^{[NO]f}/_{[NO]i}\}$$

where, [NO]f = Exit Concentration (ppm)
[NO]i = Inlet Concentration (ppm).

Inspection of Figure 4 shows conversion increasing as a function of temperature. The conversion varies from approximately 10-70% over the temperature range 870-960 °C.

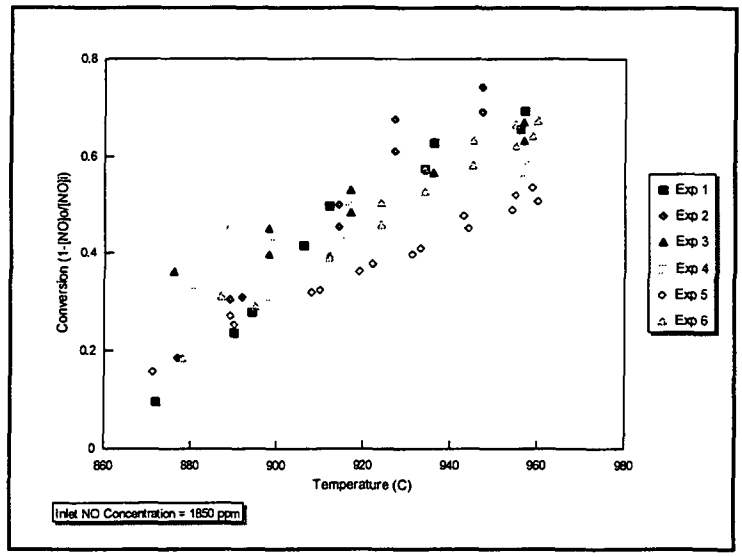

Figure 4: Conversion as a Function of Temperature

The depletion of NO by reaction with molten sodium carbonate has been assumed to follow a first-order kinetic expression,

$$-r = k\,[NO].$$

Manipulation of this expression leads to the following:

$$\ln(a/t) = \ln(k_o) - Ea/RT,$$

where, $a = -\ln(^{NOf}/_{NOi})$
Ea = Activation Energy (kJ)
T = Absolute Temperature (K)
t = Time (sec)
k = Arrhenius rate constant = $k_o\, e^{-Ea/RT}$
k_o = Pre-exponent for rate constant

If the data do indeed follow first-order kinetics, then a plot of ln(a/t) *vs.* 1/T should yield a straight line with a slope of -Ea/R. A plot of this type is shown below in Figure 5 for Experiment 5.

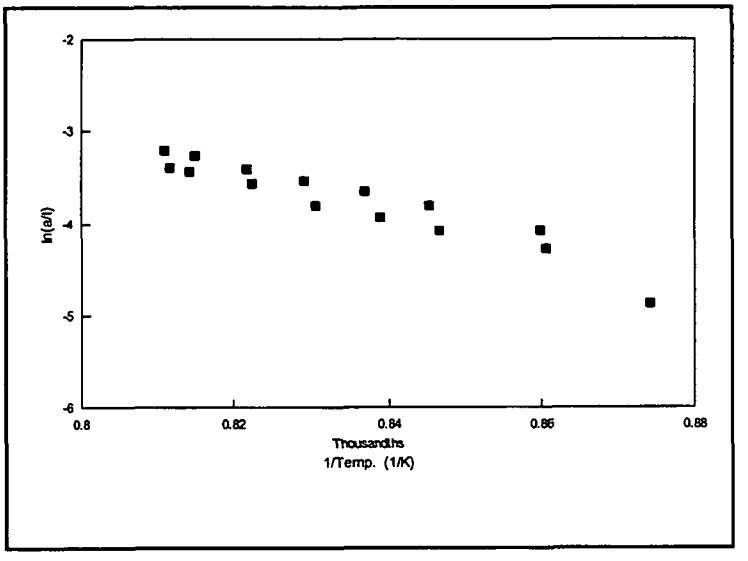

Figure 5: Graphic Representation of Experiment 5; Assumed First-Order Kinetics

Visual inspection of Figure 5 reveals a linear fit of the data. Linear regression on all six experiments gives the results shown in Table 3.

Table 3: Regression Output for Assumed First-Order Kinetics

Experiment	1	2	6	3	4	5
Mass of Na_2CO_3 (g)	35	35	35	17.5	17.5	17.5
Slope: -Ea/R	-36,120	-36,640	-29,240	-17,280	-16,160	-21,540
Y - Intercept: $ln(k_o)$	26	26.7	20.2	11.2	10	14.2
R-Squared	0.856	0.931	0.944	0.949	0.932	0.903

Table 3 shows R-squared values ranging from .85-.95 which indicate a fairly good fit of the data. (A value of R-squared = 1 indicates a perfect fit). Based on this data it would appear that the assumption of first-order kinetics is correct; however, the calculated activation energies are not constant for the

different experimental conditions. For the experiments conducted with the lighter mass of salt, the average activation energy (152 kJ) is about half the calculated value (283 kJ) for the other set of experiments. A change in activation energy by a factor of two usually indicates mass transfer limitations. It is possible that for the lighter mass of salt, the gas contacting pattern is different. There may be channeling of flow or excessive splashing.

Discussion

Preliminary results show that NO does indeed react with molten sodium carbonate. A conversion of 10-70% was observed over the temperature range of 860-970 °C. The reaction seems to follow first-order kinetics; however, mass transfer limitations appear to occur for at least half of the experiments. Further work must be conducted to eliminate mass transfer control before a true kinetic expression can be developed.

Sodium carbonate has been chosen as the starting material for the first phase of this study. Once a reaction rate has been determined, sodium sulfide (Na_2S) and sodium sulfate (Na_2SO_4) can be added to more closely simulate recovery furnace smelt. Work is also planned to investigate the effect of inlet concentration and the presence of other gases such as O_2 and SO_2.

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